

PATENT ABSTRACTS OF JAPAN

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(54) POSITIVE PHOTSENSITIVE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive photoresist composition capable of forming a resist pattern superior in adhesion with a substrate, above all, the substrate obtained by forming a thin film made of metal oxide or sulfide or the like formed by vapor deposition or sputtering on a glass plate.

SOLUTION: This photoresist composition is prepared by adding at least one of N-containing heterocyclic compounds selected from 8-oxyquinoline derivatives and 4-hydroxypteridine derivatives and 1,10-phenanthroline derivatives and 2,2'-bipyridyl derivatives to the photosensitive composition composed of a compound having a quinonediazido group.

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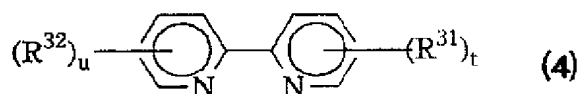
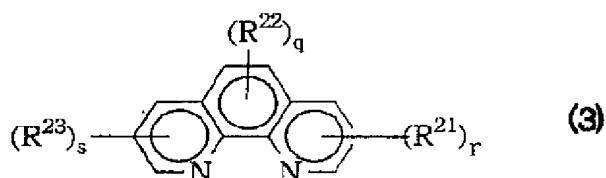
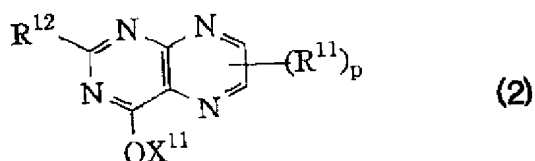
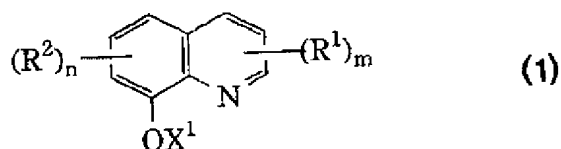
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CLAIMS

[Claim(s)]

[Claim 1] The positive type photoresist constituent characterized by making at least
one sort of nitrogen-containing heterocycle compounds chosen as the photosensitive
constituent which consists of a quinone diazide radical content compound from the
compound of general formula (1) - (4) contain.

[Formula 1]



X1 and X11 in a formula may be the same, or may differ from each other, a hydrogen atom, an acyl group, or an alkyl group is expressed, respectively, R1, R2, and R11, R12, R21, R22, R23, R31 and R32 may be mutually the same, or may differ from each other, and they express a hydrogen atom, a hydroxyl group, a carboxyl group, a sulfonic group, an alkyl group, the amino group, a halogen atom, or a sulfhydryl group, respectively. Moreover, m, n, r, and s express the integer of 0, or 1-3, respectively, p and q are 0, 1, or 2, respectively, and t and u express the integer of 0, or 1-4, respectively.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive type photoresist

constituent which can form the resist pattern excellent in adhesion with the substrate which made thin films, such as metal substrates, such as a new positive type photoresist constituent, still more detailed silicon substrate and chromium effective in manufacture of a semiconductor device, TFT (thin film transistor), etc., a tantalum, and copper, a glass substrate, and a metallic-oxide metallurgy group sulfide, form by vacuum evaporation or sputtering on glass.

[0002]

[Description of the Prior Art] The method of micro processing by the photoetching method being performed, forming the thin film of a photoresist constituent on metal substrates, such as a silicon substrate, chromium, molybdenum, and a tantalum, in manufacture processes, such as semiconductor devices, such as IC and LSI, a printed circuit board, TFT, or a liquid crystal display component, and etching this substrate on it conventionally, by using as a protective coat the resist pattern which developed negatives after irradiating activity beams of light, such as ultraviolet rays, through the mask pattern, and was obtained is taken. It is known that a quinone diazide radical content compound and the positive type photoresist constituent which combined the sensitization component which consists of a quinone diazide radical content benzophenone system compound especially are suitable for the alkali fusibility novolak mold resin for coat formation as a photoresist constituent used in this approach (for example, a U.S. Pat. No. 4377631 specification, JP,62-35349,A, JP,1-142548,A, JP,1-179147,A).

[0003] By the way, the property in which the exposure part of an activity beam of light hardens and insolubilizes is used for a photoresist, and the thing of the negative mold which forms a resist pattern, and the thing of the positive type which forms a resist pattern by carrying out dissolution removal of the exposure part with a developer conversely are known by carrying out dissolution removal of the non-irradiated part with a developer. Since a positive type photoresist is excellent in the piece and resolution of an image compared with a negative-mold photoresist, is not influenced by oxygen at the time of the exposure of an activity beam of light and is excellent also in the stability after spreading, it attracts attention as what can respond to detailed-ization of a processing dimension.

[0004] However, in addition to the resolution which a positive type photoresist has, in order to correspond to detailed-ization of this processing dimension, adhesion with a substrate substrate is very important, and to have stuck strongly is demanded, without a detailed resist pattern exfoliating easily from a substrate substrate during processing of development, etching, etc. The conventional positive type photoresist is

not enough and it is impossible to correspond to detailed-ization of a processing dimension in this point. In order to raise the adhesion over the substrate substrate of this positive type photoresist What added partial saturation dicarboxylic acid and the compound obtained from ethylene glycol by the polycondensation reaction to the positive type photoresist (JP,59-172643,A), The positive type photoresist which arranged the precursor and the poly benzimidazole derivative of the poly benzooxazole (JP,4-46345,A), The thing (JP,5-82935,A) which added the benzotriazol carboxylic-acid derivative to the positive type photoresist, or the thing (JP,6-28657,A) which added the benzimidazole derivative to the positive type photoresist is known. The polyester compound which raises adhesion with a substrate, and the heterocycle compound are found out so that these examples may see. However, it does not necessarily have sufficient adhesion to a substrate substrate, but, in addition, adhesion improvement effects are especially insufficient, in order to correspond to detailed-ization of a current processing dimension also in these things to a metallic-oxide metallurgy group sulfide substrate. Moreover, development nature of a positive type photoresist is worsened, and the exposure part of an activity beam of light is not completely removed by the developer in the case of a development, but it has the new trouble of producing the resist remainder.

[0005]

[Problem(s) to be Solved by the Invention] This invention is made for the purpose of offering the positive type photoresist constituent which can form the resist pattern excellent in adhesion with a substrate substrate. It aims at especially offering the positive type photoresist constituent which can form the resist pattern which was excellent not only in metal substrates, such as silicon and a tantalum, but adhesion with the substrate which made the thin film of a glass substrate metallurgy group oxide and metallic sulfide form by vacuum evaporation or sputtering on glass.

[0006]

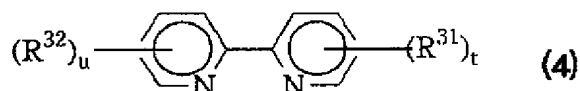
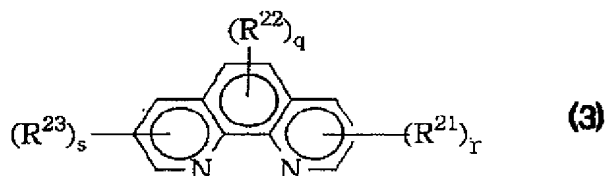
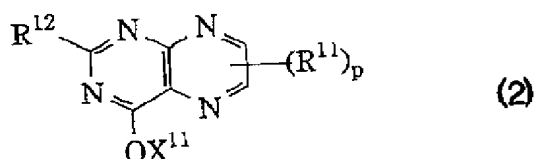
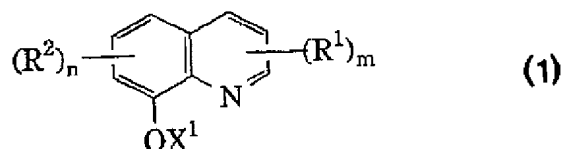
[Means for Solving the Problem] this invention persons came to complete this invention for having the effectiveness in which especially the specific nitrogen-containing heterocycle compound was excellent to the constituent which made o-quinone diazide compound the fundamental component about the positive type photoresist constituent which used o-quinone diazide compound as a result of repeating examination for the addition effectiveness of various kinds of nitrogen-containing heterocycle compounds wholeheartedly, in order to raise adhesion with a substrate substrate based on a header and this knowledge.

[0007] That is, this invention is a positive type photoresist constituent characterized

by making at least one sort of nitrogen-containing heterocycle compounds chosen as the photosensitive constituent which consists of a quinone diazide radical content compound from the compound of general formula (1) - (4) contain.

[0008]

[Formula 2]



[0009] general formula (1) - (4) -- setting -- X1 And X11 may be the same, or may differ, a hydrogen atom, an acyl group, or an alkyl group is expressed, respectively, desirable acyl groups are radicals of carbon numbers 2-4, such as an acetyl group, a propionyl radical, and a butyryl radical, and desirable alkyl groups are radicals of the carbon atomic numbers 1-3, such as a methyl group, an ethyl group, i-propyl group, and n-propyl group. R1, R2, and R11, R12, R21, R22, R23, R31 and R32 may be mutually the same, or may differ from each other, and they express a hydrogen atom, a hydroxyl group, a carboxyl group, a sulfonic group, an alkyl group, the amino group, a halogen atom, or a sulfhydryl group, respectively. When R1, R2, and R11, R12, R21, R22, R23, R31 and R32 express an alkyl group, a desirable alkyl group is a radical of

the carbon atomic numbers 1-3, such as a methyl group, an ethyl group, i-propyl group, and n-propyl group. When it expresses a halogen atom, desirable halogen atoms are a chlorine atom, a bromine atom, and an iodine atom. When it expresses the amino group, the amino group may be permuted by alkyl groups of carbon numbers 1-3, such as 1 or two methyl groups, an ethyl group, i-propyl group, and n-propyl group. Moreover, m, n, r, and s express the integer of 0, or 1-3, respectively, p and q are 0, 1, or 2, respectively, and t and u express the integer of 0, or 1-4, respectively. When m, n, p, q, r, and s are two or more integers, two or more of the substituents may not be the same.

[0010] General formula (1) Although the desirable compound of - (4) is shown below, the compound of this invention is not limited to these.

(1) 6-methyl-8-hydroxyquinoline (2) 6-ethyl-8-hydroxyquinoline (3) 5-methyl-8-hydroxyquinoline (4) 8-hydroxyquinoline (5) 8-acetyloxy quinoline (6) 4-hydroxy pteridine (7) 2, 4-dihydroxy pteridine (8) 4-hydroxy pteridine-2-sulfonic acid (9) 2-ethyl-4-hydroxy pteridine (10) 2-methyl-4-hydroxy pteridine (11) 1, 10-phenanthroline (12) 5, the 6-dimethyl -1, 10-phenanthroline (13) 3, the 8-dimethyl -1, 10-phenanthroline (14) 3, 8-dihydroxy -1, 10-phenanthroline (15) The 5-carboxy -1, 10-phenanthroline (16) 5, 6-dihydroxy -1, 10-phenanthroline (17) 1, a 10-phenanthroline-5-sulfonic acid (18) 4, the 4'-dimethyl -2, a 2'-bipyridyl (19) — a 2 and 2'-bipyridyl (20) — 2, 2'-bipyridyl-5-carboxylic-acid (21) 5, and 5' - dichloro -2, 2'-bipyridyl (22) 3, and 3' - dihydroxy -2, 2'-bipyridyl (23) 3, and 3' - dimercapto-2 and 2' - bipyridyl [0011] Especially desirable compounds are a 4-hydroxy pteridine, 1, 10-phenanthroline, 2, and 2'-bipyridyl, 8-hydroxyquinoline, and 8-acetyloxy quinoline among the above-mentioned instantiation compounds.

[0012] Among these compounds, a 8-hydroxyquinoline derivative heats the quinoline which corresponds according to a conventional method to a potassium hydroxide and 200-250-degreeC on anhydrous conditions, or o-nitro ***** leather acid is returned and it is obtained. A 4-hydroxy pteridine derivative makes 4 and 5-diamino pyrimidine which corresponds according to a conventional method, and a glyoxal react, and is obtained. Moreover, according to a conventional method, 1, 10-phenanthroline derivative and 2, and a 2'-bipyridyl derivative also make a substituent add to 1, 10-phenanthroline and 2, and a 2'-bipyridyl, respectively, and are obtained.

[0013] Compound (1) The addition of - (4) is for 0.1 - 5 % of the weight preferably 0.01 to 15% of the weight to the formed element of a constituent, although the optimal range changes with the class of substrate, and contents of the constituent.

[0014] By adding the compound chosen from compound [of this invention] (1) - (4) in

a photoresist constituent, adhesion with a substrate improves remarkably, advance of side etch is prevented in process of micro processing of the pattern protected by the photoresist in connection with it, and the precision of a pattern is maintained. When calling it a substrate by this invention, the layer which touches the resist constituent of this invention directly is pointed out, and there is also a thing of the layer of the thin film material for patterning which it may be the base material itself, such as a metal plate and a glass plate, and was prepared with means, such as vacuum evaporation and painting, on the base material. The substrate especially with the big effectiveness of this invention is a substrate which made the thin film of a metallic sulfide metallurgy group oxide form by vacuum evaporation or sputtering on glass. Although there was especially no means to improve adhesion when metallic sulfide was conventionally used as a substrate, especially this invention is suitable for this purpose. In addition, if it adds for a sense, use of an annular hydroxy compound is indicated by JP,60-11344,B for the adhesion amelioration to the base material of a photosensitive reproduction material, and 8-hydroxyquinoline is also indicated in it. However, this base material is an aluminum plate and, as for this invention, also in an object substrate, Field of application differs also from an operation gestalt.

[0015] In the constituent of this invention, a quinone diazide radical content compound is used as a photosensitive component. As this quinone diazide radical content compound, a full esterification object, a partial esterification object, etc. with polyhydroxy benzophenones, such as a 2, 3, 4-trihydroxy benzophenone, 2, 3 and 4, and 4'-tetra-hydroxy benzophenone, a naphthoquinone -1, a 2-diazido-5-sulfonic acid or a naphthoquinone -1, and a 2-diazido-4-sulfonic acid can be mentioned, for example.

[0016] Moreover, other quinone diazide radical content compounds, for example, alt.benzoquinone diazido, Alt.naphthoquinonediazide, alt.anthraquinone diazido or alt.naphthoquinonediazide sulfonates, and these nuclear substitution derivatives, The compound which furthermore has orthoquinone diazide sulfonyl chloride, a hydroxyl group, or an amino group, For example, a phenol, p-methoxy phenol, dimethylphenol, A hydroquinone, bisphenol A, a naphthol, a pyrocatechol, pyrogallol, A resultant with the pyrogallol monomethyl ether, pyrogallol -1, 3-wood ether, a gallic acid, the gallic acid that left a part of hydroxyl group, and was esterified or etherified, an aniline, p-amino diphenylamine, etc. can be used. These may be used independently and may be used combining two or more sorts.

[0017] These quinone diazide radical content compounds can be manufactured by

carrying out condensation of said polyhydroxy benzophenone, and a naphthoquinone -1, 2-diazido-5-sulfonyl chloride or a naphthoquinone -1 and 2-diazido-4-sulfonyl chloride into suitable solvents, such as dioxane, under existence of alkali, such as triethanolamine, carbonic acid alkali, and carbonic acid hydrogen alkali, and perfect-esterifying or partial esterifying.

[0018] In this invention constituent, alkali fusibility resin is used as a binder, i.e., matter for coat formation. About this alkali fusibility resin, there is especially no limit and the alkali fusibility resin commonly used as matter for coat formation can be conventionally used in a positive type photoresist constituent. As alkali fusibility resin concerning this invention For example, novolak resin, hydrogenation novolak resin, acetone-pyrogallol resin, o-polyhydroxy styrene, m-polyhydroxy styrene, p-polyhydroxy styrene, Hydrogenation polyhydroxy styrene, a halogen, or alkylation polyhydroxy styrene, A hydroxystyrene-N-permutation maleimide copolymer, o/p-, and a m/p-hydroxystyrene copolymer, the part to the hydroxyl group of polyhydroxy styrene -- o-alkylation object for example, 5-30-mol % o-methylation object and o-(1-methoxy) ethylation object -- o-(1-ethoxy) ethylation object, an o-2-tetrahydropyranyl ghost, o-acylation objects, such as o-(t-butoxycarbonyl) methylation object For example, (5 - 30-mol % o-acetylation object, o-(t-butoxy) carbonylation object), etc., Although a styrene maleic anhydride copolymer, a styrene-hydroxystyrene copolymer, an alpha-methyl-styrene-hydroxystyrene copolymer, carboxyl group content methacrylic system resin, and its derivative can be mentioned, it is not limited to these.

[0019] especially desirable alkali fusibility resin -- a part of novolak resin and o-polyhydroxy styrene, m-polyhydroxy styrene, p-polyhydroxy styrene and these copolymer, alkylation polyhydroxy styrene, and polyhydroxy styrene -- they are o-alkylation or o-acylation object, a styrene-hydroxystyrene copolymer, and an alpha-methyl-styrene-hydroxystyrene copolymer.

[0020] Novolak resin is resin to which condensation of phenols and the aldehydes was carried out under acid conditions. The novolak resin obtained, for example from a phenol and formaldehyde as desirable novolak resin, The novolak resin obtained from m-cresol, the novolak resin and p-cresol which are obtained from formaldehyde, and formaldehyde, The novolak resin obtained from o-cresol and formaldehyde, the novolak resin obtained from octyl phenol and formaldehyde, The novolak resin obtained from m-/p-mixing cresol and formaldehyde, The novolak resin obtained from the mixture and formaldehyde of a phenol/cresol (any of m-, p-, o- or m-/p-, m-/o-, and o-/p-mixing are sufficient) is mentioned. As a predetermined monomer, a phenol,

m-cresol, p-cresol, Cresol, such as o-cresol, 2, 5-xylenol, 3,5-xylenol, Xylenols, such as 3, 4-xylenol, 2, and 3-xylenol m-ethylphenol, p-ethylphenol, o-ethylphenol, Alkylphenols, such as p-t-butylphenol, p-octyl phenol, 2 and 3, and a 5-trimethyl phenol p-methoxy phenol, m-methoxy phenol, 3, 5-dimethoxy phenol, 2-methoxy-4-methyl phenol, an m-ethoxy phenol, a p-ethoxy phenol, An m-propoxy phenol, a p-propoxy phenol, an m-butoxy phenol, Bis-alkylphenols, such as alkoxy phenols, such as a p-butoxy phenol, and a 2-methyl-4-isopropyl phenol independent in hydroxy aroma compounds, such as m-chlorophenol, p-chlorophenol, o-chlorophenol, a dihydroxy biphenyl, bisphenol A, phenylphenol, resorcinol, and a naphthol, — or, although two or more kinds can use it, mixing It is not limited to these. [0021] As aldehydes, for example Formaldehyde, a paraformaldehyde, An acetaldehyde, propionaldehyde, a benzaldehyde, phenylacetaldehyde, alpha-phenylpropyl aldehyde, beta-phenylpropyl aldehyde, Ortho hydroxybenzaldehyde, an m-hydroxy benzaldehyde, A p-hydroxy benzaldehyde, o-chlorobenzaldehyde, m-chlorobenzaldehyde, p-chlorobenzaldehyde, o-nitro benzaldehyde, m-nitro benzaldehyde, p-nitro benzaldehyde, o-methyl benzaldehyde, m-methyl benzaldehyde, Although p-methyl benzaldehyde, p-ethyl benzaldehyde, a p-n-butyl benzaldehyde, a furfural, chloroacetaldehyde, and these acetal objects, for example, a chloroacetaldehyde diethyl acetal etc., can be used In these, it is desirable to use formaldehyde. These aldehydes are independent, or they are combined two or more kinds and used. As an acid catalyst, a hydrochloric acid, a sulfuric acid, a formic acid, an acetic acid, oxalic acid, etc. can be used.

[0022] In this way, as for the weight average molecular weight of the obtained novolak resin, it is desirable that it is the range of 1,000–30,000. Less than by 1,000, if the film decrease after the development of an unexposed part is large and exceeds 30,000, a development rate will become small. Weight average molecular weight is 800–200,000, and the thing of 400–60,000 has [especially a suitable thing] desirable number average molecular weight. Moreover, these novolak resin may be used only by one kind, or may be used combining two or more kinds. moreover, the weight average molecular weight of alkali fusibility resin, such as said polyhydroxy styrene other than novolak resin and its derivative, and a copolymer, — 2000 or more — desirable — 5000–200000 — it is 10000–100000 more preferably. Moreover, from a viewpoint of raising the thermal resistance of the resist film, 25000 or more are desirable. Here, weight average molecular weight has the polystyrene reduced property of gel permeation chromatography, and is defined. The amount of the above whole alkali fusibility resin used is 0 – 30 % of the weight preferably zero to 70% of the weight on

the basis of the total weight (except for a solvent) of a resist constituent.

[0023] this invention constituent can be made to carry out addition content of the component used [sensitizer / the coloring agent for making much more legible the resin, the plasticizer, the stabilizer, or the developed image for improving the engine performance of the additive which has compatibility in the system of a constituent if needed further, for example, the resist film, etc., / for raising the sensitization effectiveness more] commonly.

[0024] within the limits for which the rate of both in the case of making alkali fusibility resin and a quinone diazide radical content compound into under a basic presentation in this invention constituent is usually used -- it is -- ****ing -- usually -- the former 100 weight section -- receiving -- the latter 5 - the 200 weight sections -- it is within the limits of the 20 - 100 weight section preferably. When there is too much this alkali fusibility resin, it is inferior to the fidelity of an image, imprint nature falls, if too few, the homogeneity of the resist film will worsen, and the inclination for resolution to also decline is seen.

[0025] moreover, the loadings of compound [of this invention which is an adhesion improver] (1) - (4) -- per 100 weight sections of the solid constituent whole quantity, and 0.01 - 15 weight section -- it is preferably chosen in the range of 0.5 - 5 weight section. Since an adhesion enhancing effect will not be acquired considering an amount but sensibility will also fall if an adhesion enhancing effect is not fully demonstrated under in the 0.01 weight section and this amount exceeds 15 weight sections, it is not desirable.

[0026] As for this invention constituent, it is desirable to use the various addition components used if needed alkali fusibility resin, a quinone diazide radical content compound, the compound of general formula (1) - (4), and others described above in the form of the solution which dissolved in the suitable solvent.

[0027] As an example of such a solvent, an acetone, a methyl ethyl ketone, a cyclohexanone, Ketones, such as methyl isoamyl ketone, 1 and 1, and a 1-trimethyl acetone The monomethyl ether of ethylene glycol and ethylene glycol mono-acetate, jetty reg recall, or diethylene-glycol mono-acetate, Polyhydric alcohol, such as the monoethyl ether, the monopropyl ether, the monobutyl ether, or the monophenyl ether, and the derivative of those, Ester, such as ring type ether like dioxane, and ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, pyruvic-acid ethyl, 3-methoxy methyl propionate, 3-ethoxy ethyl propionate, can be mentioned. These may be used independently, and may mix and use two or more sorts.

[0028] As a substrate substrate which applies the constituent of this invention A

tantalum, molybdenum, chromium, iron, zinc, nickel, iron, an indium, Although substrates, such as sheets plastic, such as metals, such as copper, and an alloy of those, its oxide, its sulfide, glass, and polyester, or a silicon wafer used for manufacture of a semiconductor device, can be mentioned As opposed to the substrate which compound [of this invention] (1) – (4) made form the thin film of a metallic sulfide metallurgy group oxide by vacuum evaporation or sputtering on glass Since it has high adhesion especially, it is very effective in manufacture of the circuit boards, such as a liquid crystal display panel and a plasma-display panel. The constituent of this invention is applied on a substrate substrate using a roll coater, a dip coater, a spinner, etc., and irradiates an activity beam of light alternatively through a necessary subject-copy film after desiccation with a low pressure mercury lamp, a high pressure mercury vapor lamp, an ultrahigh pressure mercury lamp, the arc light, a xenon lamp, etc. As an alkaline water solution, for example, alkali chemicals, subsequently, a sodium silicate, A potassium silicate, a sodium hydroxide, a potassium hydroxide, a lithium hydroxide, The 3rd sodium phosphate, the 2nd sodium phosphate, the 3rd ammonium phosphate, Inorganic alkali, such as the 2nd ammonium phosphate, a sodium carbonate, potassium carbonate, and sodium bicarbonate, By carrying out dissolution removal of the exposure part of an activity beam of light with the water solution using organic alkali, such as a low-grade amine, monoethanolamine, diethanolamine, triethanolamine, and TETORAMECHIRUAMMONIUMUHIDOROKISHI On a substrate substrate, the resist pattern which was extremely excellent in adhesion can be formed.

[0029]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited to these examples.

[0030] [Example 1] What mixed m-cresol and p-cresol by the weight ratio 6:4 is used. With a conventional method The manufactured naphthoquinone -1 of 100g (weight average molecular weight 12000) of cresol novolak mold resin, and a 2, 3, 4, and 4'-tetra-hydroxy benzophenone and 4g of instantiation compounds of 30g of 2-diazido-5-sulfonates, and Table 1 The positive type photoresist solution dissolved and prepared to ethylene-glycol-monoethyl-ether-acetate 400g After carrying out spinner spreading so that it may become 3.00 micrometers of thickness on the metal substrate which made chromium vapor-deposit on a glass support plate, And it exposed using contact aligner PLA-500F (canon company make) through the test pattern mask of a Rhine and a tooth space with a line breadth of 20.0 micrometers. [on the hot plate] [110 degrees C] [for 90 seconds]

[0031] Subsequently, after removing the exposure part and forming a resist pattern on chromium by carrying out a dipping for 65 seconds into a 2.38-% of the weight tetramethylammonium hydroxide water solution, chromium was etched into fluoric acid and a nitric-acid system etching reagent 3 minutes or by carrying out a dipping for 5 minutes, having used the resist pattern as the mask for the chromium which, and was exposed. [on the hot plate] [130 degrees C] [for 3 minutes] Subsequently, in order to remove a resist and to evaluate adhesion with chromium, the result of having measured the line breadth of the pattern on chromium with the electron microscope is shown in Table 1. It was checked that all enter among 17.0-20.0 micrometers, and have good adhesion also in a detailed resist pattern. Moreover, the development remainder of a resist was not seen on the tooth space.

[0032] [Example -1 of a comparison] The result of having estimated similarly the adhesion of the resist pattern of an example 1 and the example 1 of a comparison formed by the completely same actuation as the example was also shown in Table 1 except not blending the compound concerning this invention in an example 1. It was shown by this result that thin ** of line breadth arises and enters by side etch.

[0033]

[Table 1]

(表1)

例示化合物	エッチング 時間	線幅	レジストの現像残り	備考
(4)	5分	18.9	なし	本発明
(6)	5分	18.0	なし	本発明
(11)	5分	17.5	なし	本発明
(19)	5分	17.0	なし	本発明
—	5分	15.0	なし	比較例

(注) 線幅の単位は、ミクロン。

[0034] [An example 2 and example 2 of a comparison] Except having considered as the compound substrate which vapor-deposited the zinc sulfide layer and formed the substrate substrate on glass, the resist pattern was made to form by the same actuation as an example 1, and the line breadth behind an etching mask was observed. A result is shown in Table 2. Moreover, the result of having evaluated similarly the adhesion of the resist pattern formed by the completely same actuation as the

example 1 of a comparison was also shown in Table 2 except having made the substrate substrate into the same thing as an example 2 as an example 2 of a comparison.

[0035]

[Table 2]

(表 2)

例示化合物	エッチング 時間	線幅	レジストの現像残り	備考
(4)	20分	95.2	なし	本発明
(6)	20分	90.3	なし	本発明
(11)	20分	87.1	なし	本発明
(19)	20分	81.2	なし	本発明
—	20分	50.1	なし	比較例

(注) 線幅の単位は、ミクロン。

[0036] [Example -3] One mol of isoamyl gallates, a naphthoquinone -1, the two mols [of 2-diazo-5-sulfonic-acid chloride] condensate 20 weight section, Phenol novolak resin PR-1050 (product made from Sumitomo DEYUREZU) 50 weight section, The cashew denaturation novolak resin 17BB(cashew company make) 10 weight section, The polyvinyl-methyl-ether Lutonal M-40 20 (BASF A.G. make) weight section, The 8-hydroxyquinoline (commercial thing) 1.5 weight section The ethylene-glycol-monoethyl-ether-acetate 150 weight section, It dissolved in the mixed solution which consists of the methyl-ethyl-ketone 100 weight section and the ethylene-glycol-monomethyl-ether 50 weight section, and the coating liquid of a positive type photopolymer constituent was obtained by filtering. Subsequently, after having applied the above-mentioned coating liquid using the dip coater by having used as the substrate substrate the zinc sulfide prepared at 0.8-micrometer thickness on the commercial 0.15mm thickness nickel-iron alloy material degreased and washed with the alkaline-degreasing agent and the dilute sulfuric acid, glass, and glass, respectively so that desiccation thickness might be set to 1.5 micrometers, and drying, the activity beam of light was irradiated through the positive film with 3kW ultrahigh pressure mercury lamp. Subsequently, the image stabilized by being immersed in a tetramethylammonium hydroxide water solution for 60 seconds 2.38% of the weight was obtained. And when the resist development remainder after development was

observed, all are resolved even for the tooth-space pattern of 10-micrometer width of face, and the development remainder of a resist was not seen on the tooth space. Moreover, when the same experiment was conducted using what considers as the example of a comparison and does not blend 8-hydroxyquinoline, the development remainder of a resist was checked in the tooth-space pattern below 40-micrometer width of face. The height of the development nature of this invention constituent was checked by this.

[0037] [Example -4] The coating liquid of a positive type photopolymer constituent was obtained by dissolving in the mixed solution which consists of the ethylene-glycol-monoethyl-ether-acetate 350 weight section and the ethylene-glycol-monomethyl-ether 50 weight section, and filtering 2, 3, one mol of 4-trihydroxy benzophenones and a naphthoquinone -1, the two mols [of 2-diazido-5-sulfonic-acid chloride] condensate 25 weight section, the phenol novolak resin PSF-2805 (Gunei Chemical Industry Co., Ltd. make) 75 weight section, and the 4-hydroxy pteridine 0.5 weight section. Subsequently, after having applied the above-mentioned coating liquid to the substrate in which the indium oxide coat of 400A thickness was formed on the glass substrate so that desiccation thickness might be set to 1.5 micrometers with a spinner, and drying, the activity beam of light was irradiated through the positive film with 3kW ultrahigh pressure mercury lamp. Subsequently, after developing negatives for 60 seconds and washing in cold water enough at 23 degrees C with a 2.38 weight sections % tetramethylammonium hydroxide water solution, when spray etching of the 50 degrees C of the exposed indium oxide coats was carried out for 10 minutes with the mixed solution which consists of 35% of the weight of the hydrochloric-acid 2 weight section, 60% of the weight of the nitric-acid 1 weight section, and the water 2 weight section, the etching image also with the undercut of the pattern of 20-micrometer width of face faithful to a small subject copy was obtained.

[0038] [Example -5] The condensate 40 weight section of a naphthoquinone -1, 2-diazido-5-sulfonic-acid chloride, and 1, 2, and 3-trihydroxy benzene acetone condensate, The cresol novolak resin PR-1767 (product made from Sumitomo DEYUREZU) 60 weight section, A naphthoquinone -1, the 2-diazido-4-sulfonic-acid chloride 2 weight section, The coating liquid of a positive type photopolymer constituent was obtained by dissolving in the ethylene-glycol-monomethyl-ether 400 weight section, and filtering the crystal violet powder (color by Hodogaya chemistry company) 0.75 weight section, 1, and the 10-phenanthroline 2.5 weight section. The soda glass plate of 1000-micron thickness was set into the vacuum evaporation

system, zinc sulfide was vapor-deposited in thickness of 10000A at the temperature C of 70-90 degrees under the vacuum of total pressure 5×10^{-3} Torr, and the thin film of zinc sulfide was made to form. Subsequently, after having applied the above-mentioned coating liquid to this substrate so that desiccation thickness might be set to 1.5 micrometers with a spinner, and drying, the activity beam of light was irradiated through the positive film with 3kW ultrahigh pressure mercury lamp. Subsequently, after developing negatives for 60 seconds and washing in cold water enough at 23 degrees C with a 2.38 weight sections % tetramethylammonium hydroxide water solution, the etching image faithful to a subject copy was obtained, without carrying out the undercut of the pattern of 100-micrometer width of face, when spray etching of the 25 degrees C of the exposed zinc sulfide thin films was carried out for 25 minutes with the hydrochloric-acid system etching reagent.

[0039] [Example -4 of a comparison] Other than [all] having used benzotriazol instead of 1 used in the example 5, and 10-phenanthroline, when experimented like the example 1, the resist film exfoliated and the target pattern was not obtained.

[0040]

[Effect of the Invention] The resist pattern obtained using the positive type photopolymer constituent of this invention has very high adhesion with a substrate substrate, it has the effectiveness of being hard to generate the relief from the substrate substrate of a resist pattern, peeling, side etch, etc. in the processing of etching, plating, etc. to the substrate substrate which is moreover degree process since there is also little aging and it is stable, and high quality and highly precise processing processing can do it to a substrate substrate.

[Translation done.]